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Inkjet printing as a flexible technology for the deposition of thermoelectric composite structures

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Abstract

In this work we demonstrate that thin-film thermoelectric composite structures can be easily fabricated using inkjet technology. A major advantage of this procedure is the formation of tailored composite structures from the precursor inks using a provided pattern. Depending on the structural design, the thermoelectric properties of fully Inkjet-printed single-element thermoelectric generators (TEGs) show thermoelectricity in the 10 mV range and currents in the µA range. The study represents the basic phenomena of thermoelectric composite structures despite from the magnitude of thermoelectric properties of the composite components. The precursor inks we use are poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate)-ink (PEDOT:PSS-ink), ZnO-ink and Ag-ink for the interconnects. PEDOT:PSS is a conductive polymer and forms the matrix of the composite containing different amounts of ZnO-nanoparticles. We observed nearly a doubling of the thermoelectric voltage and constant current in comparison of a PEDOT:PSS/ZnO-composite with pure PEDOT:PSS, except the two times higher resistance of a composite-based TEG. Increasing the amount of ZnO-nanoparticles leads to higher voltage but a deterioration of the resistance is also observed. With increasing values of ZnO-nanoparticles in the polymer PEDOT:PSS and ZnO-nanoparticles form strong minted separate areas like "vesicles" type with a boundary layer containing the composite. This results in a lower thermoelectrical performance because of a resulting high resistance of the TEG. Furthermore, possibilities of reducing the resistance of the composite structures could be realized by adding metal nanoparticles or simply by varying the printing process of the precursor inks.

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1. Introduction

According to a growing interest in the development of energy harvesting for electrical power supply of sensor networks, mobile devices and electrical microsystems thermoelectric materials and thermoelectric harvesting became more important especially for the cases when there is no light. The aim of nowadays researches is to provide low cost thermoelectric devices while processing a high thermoelectric efficiency. Such devices called thermoelectric generators (TEGs) are used in order to generate electricity from waste heat by converting a temperature gradient into electrical energy. The property of thermoelectric materials is providing a voltage ΔV when a temperature gradient ΔT is present, according to the Seebeck effect:

$$\Delta V = S \cdot \Delta T \tag{1}$$

where S denotes the Seebeck coefficient. The conversion efficiency of a thermoelectric material is expressed by the dimensionless figure-of-merit (ZT), defined as

$$ZT = S^2 T \sigma / \kappa \tag{2}$$

including the electrical conductivity σ, thermal conductivity κ and the absolute temperature T. High Seebeck coefficient and high electrical conductivity combined with low thermal conductivity distinguishes a good thermoelectric material [1]. Typical thermoelectric materials are inorganic semiconductors whereby some of them (e.g., Te, Bi, Pb) are toxic and expensive that their use in TEGs on large scale is not practical. These materials operating near room temperature have a ZT of about 1, e.g. BiTe-compound, and show 10% Carnot efficiency. For an efficiency of about 30%, typical for a domestic refrigerator, a ZT of about 4 is needed. According to the prediction of Hicks and Dresselhaus in 1993 [2,3] the reduction of physical dimensionality of the materials leads to enhanced thermoelectric performance. The enhanced density of states (DOS) near the band edge increase the magnitude of Seebeck coefficient and boundary scattering of phonons in a result of reduced lattice thermal conductivity κ_{ph}, while $\kappa = \kappa_{\mathrm{el}} + \kappa_{\mathrm{ph}}$, with κ_{el} the electron contribution of the thermal conductivity (e.g., p-type Bi_2Te_3/Sb_2Te_3 superlattices have a $ZT = 2.4$ [4]).
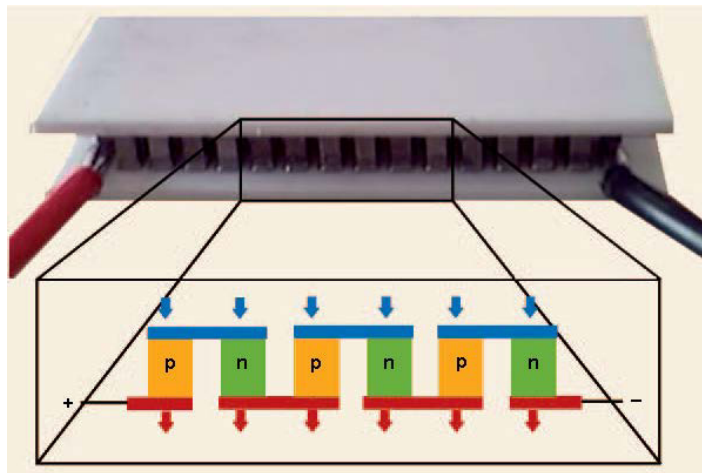

Fig. 1. Schematic drawing of a thermoelectric generator (TEG) [5].

A State-of-the-Art TEG generally consists of two solid semiconductor materials. Thereby thermoelectric couples of n-type and p-type elements are connected in series and oriented thermally parallel to a gradient (see Fig. 1).

Alternative candidates for thermoelectric materials are organic materials, more precisely conductive polymers. Their low cost and ease of processability make them interesting especially for additive manufacturing with digital printing of 2-dimensional planar arrays of thermoelectric structures. As described by Madan et al. [6], 2d-TEGs can easily be constructed by dispenser technique using metals and a semiconducting material. A semiconductor can also be a composite material. Polymers are poor thermal conductors, this makes them ideal for use as thermoelectrics, and however, their low electric conductivity and Seebeck coefficient, and stability are complicating their use in thermoelectric applications.

In this study, PEDOT:PSS, a p-type semiconductor, has been chosen because of its good solubility in water, flexibility, thermal stability, low thermal conductivity and that offers a broad spectrum of implementation possibilities. The problem of PEDOT:PSS and also other semi-conducting polymers is their insufficient thermoelectric efficiency by themselves caused by limited electrical conductivity and Seebeck coefficient. An approach to overcome the thermoelectric limitation of PEDOT:PSS can represent the use of a polymer nanocomposite where the composite consists of inorganic nanostructures of a thermoelectric material embedded in a polymer matrix with the prospect of greater thermoelectric properties of the composite than the pure polymer. There are two classes of inorganic materials to use for improving the thermoelectric properties of PEDOT:PSS. One class represents materials possessing very high electrical conductivity (e.g., graphene, carbon nanotubes (CNTs), Ag/Au/Cu-nanoparticles) and when they are incorporated in the polymer matrix the electrical conductivity of the composite can be dramatically increased, while thermal conductivity and Seebeck coefficient relatively unchanged. The other class represents inorganic materials with high Seebeck coefficient (e.g., Te, Bi_2Te_3, $Ca_3Co_4O_9$) with an improvement on the Seebeck coefficient of the composite [7,9]. In this work we use for inorganic nanostructures n-type ZnO-nanorods. Zinc oxide is not one of the best thermoelectric material, but it has a higher Seebeck coefficient of $-85~\mu V/K$ in comparison to PEDOT:PSS with 15 $\mu V/K$ at RT [7,8]. Further, we want to present the possibility of fabrication nanocomposite structures just by printing the precursor inks without any prior in-situ reactions or the use of mechanical dispersion.

2. Experimental

2.1 Device Fabrication

In order to investigate the properties of fully Inkjet-printed thin-film composite TEGs a layout has been designed for a two dimensional single element TEG with respect to a lateral temperature gradient (Fig. 2). The device consists of five single elements connected in series.
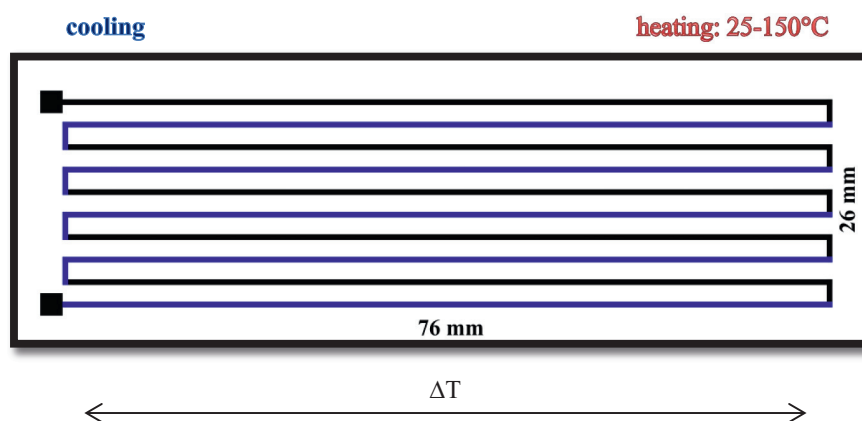

Fig. 2. Architecture of the 2-dimensional printed TEG, consisting of black: metal electrodes and interconnects, blue: TE-material/composite.

All TEGs are printed by an Inkjet printer (FUJIFILM Dimatix Materials Printer DMP-2800 Series) using microscope slides as a substrate (Thermo SCIENTIFIC) with overall dimensions of 76x26mm. The device length is given by the device application as heating and cooling need to be efficiently transferred. Before printing the substrate was cleaned in fresh 1 molar NaOH solution for 15 minutes, washed with deionized water and finally with acetone. At first the part of the pattern with blue lines (see Fig. 2) was deposited on the substrate. Followed by a thermal activation step to evaporate the fluid and to condensate the printed structure and printing the second part of the pattern with black lines. The final structure of the TEG was oven sintered at 150°C for 30 minutes ($Cu_{0.55}Ni_{0.44}Mn_{0.01}$ was sintered at 300°C for 1h with H_2-athmosphere) and sealed with a temperature-resistant lacquer (Plastik CRAMOLIN® available at CONRAD) after contact wires were fixed with conductive paste (Elecolit® available at Panacol-Elosol GmbH) at 150°C for 5 min in an oven. The following inks were used:

- silver-ink (Sigma Aldrich)
- PEDOT:PSS-ink (Sigma Aldrich)
- constantan-ink with 15wt% of $Cu_{0.55}Ni_{0.44}Mn_{0.01}$ in triethylene glycol monomethyl ether (TGME)/ ethylene glycol (EG) (protected by Fraunhofer)
- ZnO-ink with 4wt% of ZnO-nanorods [10], the calculated amount of nanorods has been dispersed in ethylene glycol using an ultrasonic bath

For electrodes and interconnects (black lines in Fig. 2) the Ag-ink and for TE-structures (blue lines see Fig: 2) PEDOT:PSS-, constantan- and ZnO-ink has been used. The composite structures were fabricated by printing 15 layers of PEDOT:PSS-ink over the ZnO-printed layers, whereby the amount of ZnO was changed by the number of printed ZnO-layers from 20wt% (2 printed layers) up to 100wt% (10 printed layers). That kind of printing process leads to a two-film system. Furthermore, for a better distribution of ZnO-nanorods in the polymer matrix varying the printing process of the precursor inks was adjusted by printing two times PEDOT:PSS-ink (7 and 8 layers) over the half of ZnO-printed layers in order to generate a four-film system. The following TEG-types were fabricated and characterized (5 means 5 elements in series):

- 2d-Silver-$(Cu_{0.55}Ni_{0.44}Mn_{0.01})_5$-TEG
- 2d-Silver-$(PEDOT:PSS)_5$-TEGs
- 2d-Silver-$(PEDOT:PSS/ZnO_n)_5$-TEGs with different amount of ZnO-nanorods from n=0.2 up to n=1 in relation to the polymer matrix

2.2 Characterization

Thermoelectric properties of printed TEGs have been characterized by a simple experimental setup: A temperature gradient realized by a cooling device, which was fabricated by soldering from sections of copper sheets, cooled by ice-water and a heating plate (IKA), has been applied on both ends on test specimens (Fig.3).
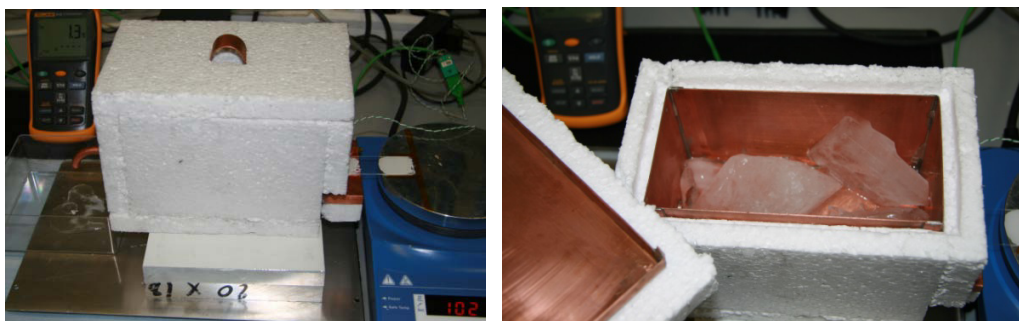

Fig. 3. Experimental setup with polystyrene insulated cooling device, heating plate and thermocouple for characterisation of the printed TEG structures.

In order to achieve a better contact between the heating plate, cooled copper plate and the TEG a thermal conductive paste was used. The temperature of the cold side (1.3-1.4°C) of the TEG structure was controlled by a thermocouple, while the temperature of the heating plate was changed in 25 degrees steps to finally 150°C. Therefore, temperature gradients ΔT of ~25, 50, 75, 100, 125 and 150 K could be implemented. At each temperature gradient converted electrical voltage, current and resistance were measured with a two-point electrical measurement system (FLUKE).

3. Results and Discussion

Fully Inkjet-printed thin-film TEG structures (see Fig. 4) show structural thicknesses of 1.4 μm for silver, 3.5 μm for pure PEDOT:PSS, 4.5 μm for $Cu_{55}Ni_{44}Mn_1$ and 4-4.5 μm for the composites. Structural widths are for all structures ~550 μm of silver, PEDOT:PSS and PEDOT:PSS/ZnO-composite and ~700 μm for $Cu_{0.55}Ni_{0.44}Mn_{0.01}$ across a length of 70 mm (measured with FRT MicroProf®).
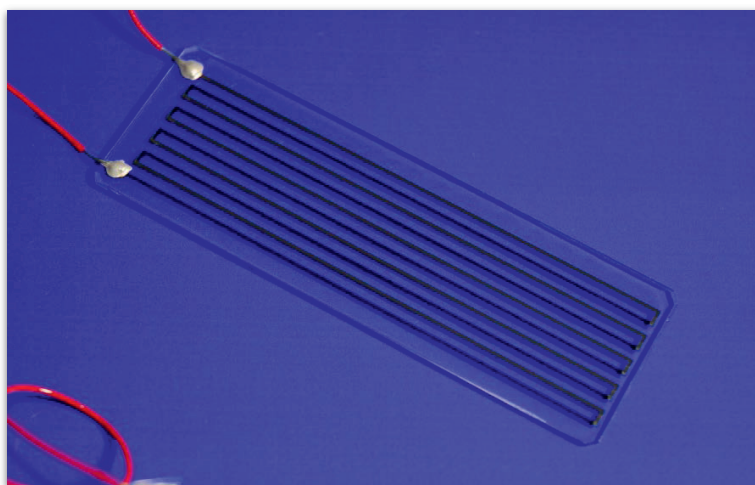

Fig. 4. Inkjet-printed thin-film TEG structure for characterisation of thermoelectric properties of used materials.

For evaluating the thermoelectric properties of the resulting composite TEG structures, it is necessary to fabricate some standard structures. For this purpose, a 2d-Silver-$(Cu_{0.55}Ni_{0.44}Mn_{0.01})_5$-TEG and a 2d-Silver-$(PEDOT:PSS)_5$-TEG serve as references. The simplest approach to convert thermal energy into electrical energy is a peltier-element consisting of two different metals with a large difference in their thermoelectric properties, e.g. silver showing a thermoelectric power of +0.67…+0,79 mV / 100K, and $Cu_{0.55}Ni_{0.44}Mn_{0.01}$ showing a thermoelectric power of -3.47… -3.04 mV / 100K [11]. The resulting thermoelectric properties of both TEG structures are listed as follows in Tab. 1:

Table 1. Resulting Inkjet-printed thermoelectric properties of 2d-Silver-$(Cu_{0.55}Ni_{0.44}Mn_{0.01})_5$-TEG and a 2d-Silver-$(PEDOT:PSS)_5$-TEG.

Material combination of the TEG	ΔT [K]	ΔU [mV]	I [μA]	R [kΩ]	P [nW]
Ag / $Cu_{0.55}Ni_{0.44}Mn_{0.01}$	100	18	9.2	0.9	360
Ag / PEDOT:PSS	100	4.9	1.1	3.8	6.4

It is easy to see that the thermoelectric properties of the $Cu_{0.55}Ni_{0.44}Mn_{0.01}$-TEG structure is 60 times higher than the same structure with PEDOT:PSS as the thermoelectric material. The reason for this observation is a bigger Seebeck coefficient -35μV/K [12] of constantan combining with a high electrical conductivity in addition to structural thickness and width, because of differences during the printing process caused by the ink. Constantan is an alloy and its thermal conductivity is much higher compared to polymers. Therefore, the electron contribution of

thermal conductivity is high, but the phonon contribution should be restricted caused by the presence of nanoparticles. Scanning electron microscope (SEM) images of cross sections show the morphology of PEDOT:PSS and constantan printed layers (see Fig. 5). They show a very homogenous and dense layer of the polymer and a very porous layer of constantan consisting of flakes in the μm-range covered by very small particles in the nm-range. For further investigations of PEDOT:PSS/ZnO-composites it must be ensured that differences of Ag/PEDOT:PSS structures in each of their performance caused by measuring tolerance and differences during the printing process is not in the range of observed parameters of the composite structures. Three fabricated Ag/PEDOT:PSS structures show a tolerance of ~3%.
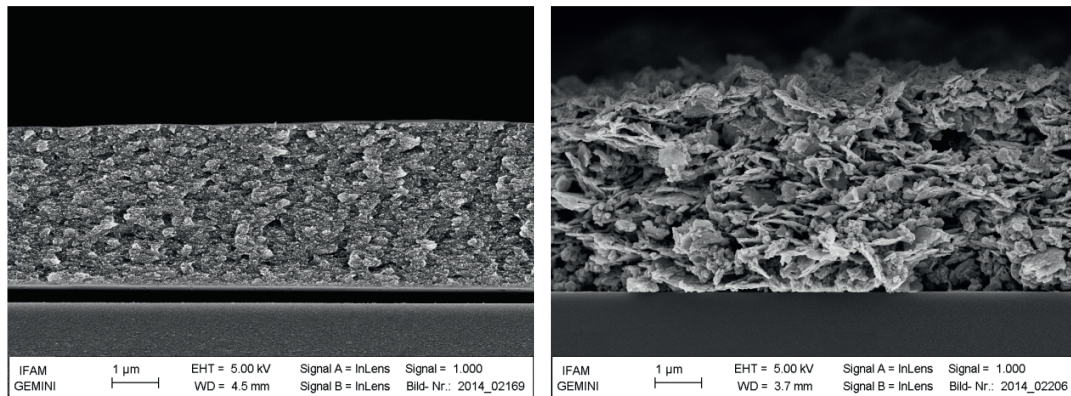

Fig. 5. SEM images of cross sections of printed PEDOT:PSS (left side) and $Cu_{0.55}Ni_{0.44}Mn_{0.01}$ (right side) structure.

The resulting thermoelectrical properties of PEDOT:PSS/ZnO$_n$-TEG structures are listed in Tab. 2:

Tabale 2. Resulting thermoelectric properties 2d-Silver-(PEDOT:PSS/ZnO$_n$)$_5$-TEGs with different amount of ZnO-nanorods and a two-film system.

| Material combination of the TEG	ΔT [K]	ΔU [mV]	I [μA]	R [kΩ]	P [nW]
Ag / PEDOT:PSS-ZnO$_{0.2}$	100	6.7	1.1	4.8	9.4
Ag / PEDOT:PSS-ZnO$_{0.4}$	100	8.9	0.9	8.9	8.9
Ag / PEDOT:PSS-ZnO$_{0.6}$	100	8.1	0.7	10.8	6.1
Ag / PEDOT:PSS-ZnO$_{0.8}$	100	8.2	0.8	9.3	7.2
Ag / PEDOT:PSS-ZnO$_1$	100	8	0.8	9.6	6.7

　　Both TEG structures with 20% and 40% of ZnO-nanorods show enhanced thermoelectricity in comparison to a pure Ag/PEDOT:PSS structure. The electric power $P = U^2/R$ increases by 28-32%. However, not only the voltage increases but at the same time the resistance of the whole structure has almost doubled. Further increase of the ZnO-nanorods proportion results in slightly enhanced electric power because of the high resistance. The devices of the four-film system show similar results with additional enhanced thermoelectricity and an increase in electric power up to 38-42%. The reason for this observation might be the distribution of the ZnO-nanorods in the polymer matrix. So in the case of sequential printing of PEDOT:PSS- and ZnO-ink a higher amount of nanorods is integrated into the composite structure (see Fig. 6). Comparing the measured current of all composite structures with the PEDOT:PSS structure (see Tab.1) no significant increase is found due to higher resistivity. Rather a small reduction of the measured current with bigger amount of nanorods and higher resistivity is observed.

Table 3. Thermoelectric properties of 2d-Silver-(PEDOT:PSS/ZnO$_n$)$_5$-TEGs with different amount of ZnO-nanorods and a four-film system.

Material combination of the TEG	ΔT [K]	ΔU [mV]	I [μA]	R [kΩ]	P [nW]
Ag / PEDOT:PSS-ZnO$_{0.2}$	100	6.9	1.2	4.3	11.1
Ag / PEDOT:PSS-ZnO$_{0.4}$	100	9.1	1	8	10.4
Ag / PEDOT:PSS-ZnO$_{0.6}$	100	8.1	0.8	10.4	6.3
Ag / PEDOT:PSS-ZnO$_{0.8}$	100	8.3	0.9	8.9	7.7
Ag / PEDOT:PSS-ZnO$_1$	100	8.1	0.8	9.2	7.2
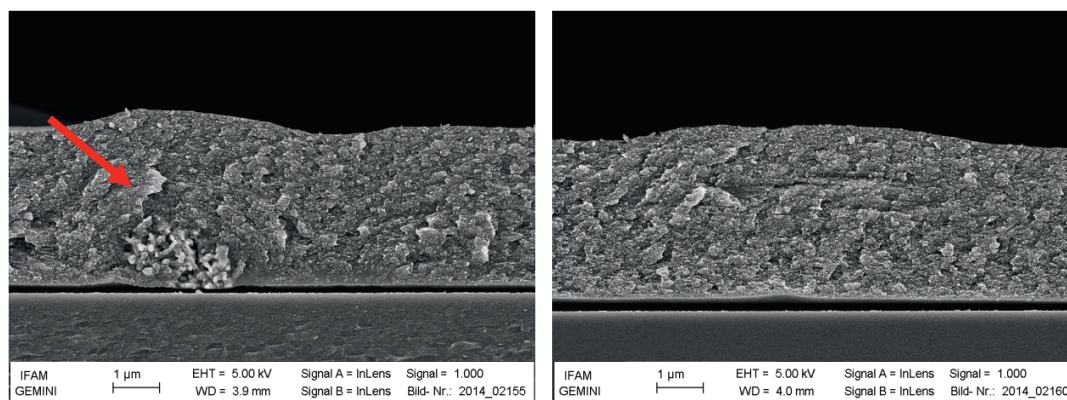
Fig. 6. SEM images of cross sections of PEDOT:PSS-ZnO0.2 composite printed as a two-film system (left side) and as a four-film.

These images show that in the case of the four-film system the composite becomes more homogenous in contrast to the printed two-film system. The latter process leads to formation of separated ZnO areas covered with the polymer. A higher magnification image indicates ZnO-nanorods in areas formed thus. Some nanorods are covered with the polymer and some of the nanorods are separately embedded in the polymer matrix. With increasing amount of ZnO-nanorods, these areas becoming larger [13], thus enhancing the resistance of the structures of both printing types.
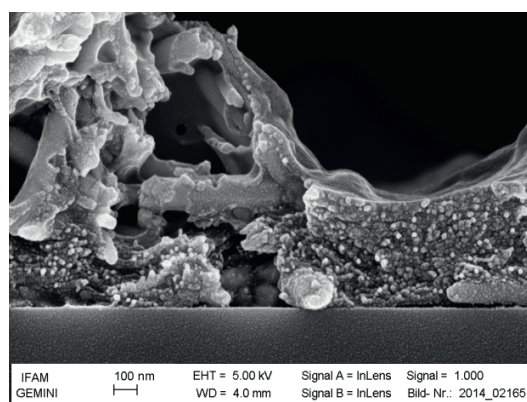
Fig. 7. SEM image of cross sections of PEDOT:PSS-ZnO$_{0.2}$ printed four-film system at an edge region of the structure.

They break out the dense polymer layer, act like electrical discontinuities and the charge carrier transport did not exclusively occur through PEDOT:PSS. In addition, four-film system composites are positively affected by a better

distribution of the nanoparticles and a slightly lower resistance of the structures. In the case of PEDOT:PSS-ZnO$_{0.2}$ printed four-film system the presence of areas, which look like "vesicles" of ZnO-nanorods, might not be excluded, they might appear more rarely and a reduced size. So they are better embedded in the polymer layer. An indication for this is the wavy texture of the polymer surface (see Fig. 5 and 6). The reason for the formation of these "vesicles" might be the coffee-ring effect [14] as well as repelling forces caused by different polarities of the solvents contained in the inks and their incompatibility with the polymer.

A possibility to reduce the high resistivity of PEDOT:PSS composites is to add graphene, carbon nanotubes (CNTs) or Ag/Au/Cu-nanoparticles. In addition, also Cu$_{55}$Ni$_{44}$Mn$_1$ nanoparticles might have promising effects in reducing the resistance of PEDOT:PSS. Anyhow, the actual results show a very high resistance and no considerable thermoelectric properties. The alloy nanoparticles seem to initiate a chemical reaction within the PEDOT:PSS material. So the polymer might have a changed structure after composite formulation. Further possibilities to reduce the resistivity of PEDOT:PSS structures are discussed in [13].

4. Conclusion

PEDOT:PSS/ZnO structures with different amount of ZnO-nanorods from 1 down to 0.2 in relation to the polymer matrix have been prepared using inkjet technology. The relative amounts of 0.2 and 0.4 show the best result in thermoelectric properties. Four-film systems show higher thermoelectricity than two-film systems. An expected optimum must be for an amount of ZnO-nanorods < 0.2 combined with a four-film system, because of evenly distributed nanorods in the polymer matrix and a reduced resistance. In the presence of using inkjet technology that could be a challenge to print nanoparticle layers with low contents and a homogenous distribution of them over the printed area. One reason is given in the stability of the nozzles and of the inks during the printing process. Another effect especially for inkjet printing is the coffee-ring effect. It rises from a convective and capillary-driven depositions of particles on a substrate during solvents evaporate.

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